Strong Electron-Phonon Coupling in δ-phase Stabilized Plutonium

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Heat capacity measurements of the δ-phase stabilized alloy $Pu_{0.95}Al_{0.05}$ suggest that strong electron-phonon coupling is required to explain the moderate renormalization of the electronic density of states near the Fermi energy. We calculated the contributions of the heat capacity from the lattice and electronic degrees of freedom, as well as from the electron-lattice coupling term, and found good overall agreement between experiment and theory assuming a dimensionless electron-phonon coupling parameter of order unity, $\lambda \sim 0.8$. This large electron-phonon coupling parameter is comparable to reported values in superconducting metals with face-centered cubic crystal structure, for example, Pd ($\lambda \sim 0.7$) and Pb ($\lambda \sim 1.5$). In addition, our analysis showed evidence of a sizable residual low-temperature entropy contribution, $S_{res} \sim 0.4\ k_B$ (per atom), which could be fit by a two-level system. Therefore, we speculated that the observed residual entropy originates from crystal-electric field effects of the Pu atoms or from self-irradiation induced defects frozen in at low temperatures.

The actinide metal plutonium (Pu) exhibits six unique crystal structures (phases) in the solid state at ambient pressure between absolute zero and its melting temperature. The phases range in symmetry from simple monoclinic (sm) to body-centered cubic (bcc). The easily worked face-centered cubic (fcc) phase, denoted by δ, is thermodynamically stable in pure plutonium from 592 K to 736 K, and can be stabilized down to room temperature by small additions of trivalent elements such as gallium or aluminum. The effects of alloying have a profound impact on the electronic structure. Specifically, the low-temperature α phase (sm) of pure Pu has an enhanced Sommerfeld coefficient of $\gamma_S = 17$ mJ/(mol K^2) compared to a simple metal with typically $\gamma_S \sim 1$ mJ/(mol K^2), while the stabilized δ phase exhibits a moderately heavy electron mass with an enhanced Sommerfeld coefficient $\gamma_S = 50$–70 mJ/(mol K^2). It is believed that the high-volume δ phase has localized, nonbinding electrons, while in the low-volume α phase the electrons are itinerant and binding. This behavior resembles the Mott transition in correlated electron systems. In a recent calorimetry study, Lashley and coworkers [1] pointed out that the low-temperature data of the heat capacity of $Pu_{0.95}Al_{0.05}$ exhibit a moderately enhanced Sommerfeld coefficient, $\gamma_S = 64$ mJ/(mol K^2), and a λ-shaped anomaly around 60 K in C/T. These observations were suggestive to those authors to describe $Pu_{0.95}Al_{0.05}$ as an incipient heavy-fermion system.

The purpose of this study [2] was to give a quantitative description of the electron-phonon interaction on the conduction electrons in a plutonium alloy, and whether the observed low-temperature λ-shaped anomaly in C/T is associated with a martensitic phase transformation. From this study we concluded that the observed anomaly was unlikely due to a full or partial martensitic phase transformation from the high-temperature δ phase into the low-temperature α′ phase (note the substitutional binary alloy α′ and α have the same crystal structure). Because on cooling this transformation finishes around 130–180 K and is completely reversed on heating around 380 K. Instead of a structural transformation, we speculated that crystal-electric field effects or self-irradiation induced defects and vacancies, for example, Frenkel pairs, are responsible for the reported excess entropy.

A direct consequence of our analysis is that the relatively strong electron-phonon

coupling of order unity, necessary for describing the measured specific heat data, would suggest that the alloy PuAl should become superconducting below a few Kelvin. So far no evidence of superconductivity has been observed down to roughly 3 K.

We followed the standard approach and divided the calculation of the total heat capacity of a metal into a vibrational, electronic, electron-phonon coupling, and residual (everything else) term, $C = C_{ph}+C_e+C_{ep}+C_{res}$. One by one, we calculated their contributions and importance. Furthermore, we assumed that the thermodynamic properties are dominated by the fcc δ-Pu crystal structure and any possible admixture of α′ is negligible.

In Fig. 1 we are comparing the combined total theoretical heat capacity with experiment. The agreement is excellent. Here we combined the individual contributions to the heat capacity, assuming an electron-phonon coupling parameter λ~0.8 with Eliashberg's $\alpha^2F(\omega)$ function that has an Einstein mode at 2.8 THz, a two-level system (TLS) with an occupation factor $n \approx 0.5$ and level splitting $T_{TLS} \approx 120$ K, as well as an electron density of states peaked at the Fermi level.

In conclusion, we studied heat capacity measurements of δ-phase stabilized PuAl alloy and calculated the vibrational, electronic, electron-phonon, anharmonic, crystal-electric field, and structural transformation contributions. Thereby, we found several important aspects: 1) electron-phonon coupling is strong and cannot be neglected at low temperatures; 2) an electronic density of states peaked at the Fermi energy with an electron-phonon coupling parameter of order unity, λ~0.8, is necessary to account for most of the electronic heat capacity; 3) a residual excess entropy of order S_{res}~0.4 k_B (per atom) can be understood in terms of an additional internal degree of freedom, for example, crystal-electric field effects or self-irradiation induced defects at plutonium sites; 4) a structural transformation from δ→α′ occurs at temperatures too high, and is too small in magnitude, to account for the low-temperature excess entropy; and 5) finally, the excess entropy and the λ-shaped anomaly in C/T are not indicative of any significant lattice anharmonicity.

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[1] J.C. Lashley et al., *Phys. Rev. Lett.* **91**, 205901 (2003).
[2] M.J. Graf et al., *Phys. Rev. B* **72**, 045135 (2005).

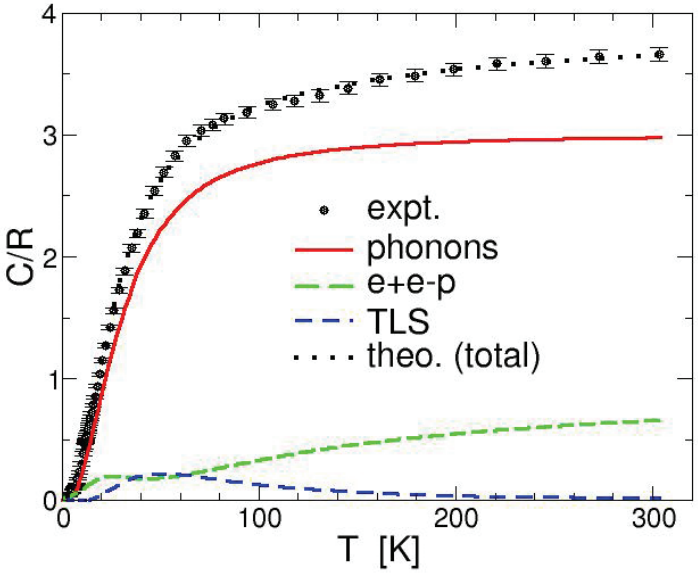

Fig. 1.
Comparison between experimental heat capacity and theory, which has been decomposed into phonon, electron-phonon renormalized electronic and two-level system contributions.